

EFFECT OF A CATALYST ON THE SOLVENT-FREE LIQUEFACTION OF DECS-17 COAL

R.P. Warzinski, B.C. Bockrath, G.A. Irdi, H.B. Booher, and A.W. Wells
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236.

Keywords: Coal liquefaction, molybdenum sulfide catalysts, reaction mechanism

INTRODUCTION

Dispersed catalysts are important factors in efforts to improve the first stage of direct coal liquefaction processes. Understanding the role of these catalysts is vital to improving their performance. Prior work at the Pittsburgh Energy Technology Center has been devoted to studying the role of a dispersed catalyst, apart from that of added solvent or vehicle, in the first stage of liquefaction (1). In that work, $\text{Mo}(\text{CO})_6$ was found to be an excellent precursor for generating dispersed MoS_2 -containing catalyst for the solvent-free liquefaction of coal.

In the work reported here, solvent-free thermal and catalytic microautoclave experiments with DECS-17 coal were performed at various residence times to investigate the role of the MoS_2 -containing catalyst formed from $\text{Mo}(\text{CO})_6$ in the initial stages of the liquefaction process. A temperature slightly above that where pronounced catalyst-induced hydrogen uptake was previously observed (375°C) was used in this study. The focus of this paper is on the characterization of the THF-insoluble products. These products were characterized by organic petrology, oxygen speciation analysis, solid-state ^{13}C NMR, and elemental analysis. A more complete account of this work and of similar experiments conducted at 350°C and 400°C is not possible here but will be reported at a later time.

EXPERIMENTAL

All experiments were performed with DECS-17 (Blind Canyon) coal from the Penn State Coal Sample Bank. The elemental analysis (on a dry basis) provided with the coal was as follows: 76.3% carbon, 5.8% hydrogen, 1.3% nitrogen, 0.4% sulfur (0.02% pyritic sulfur), 6.6% ash, and 9.7% oxygen (by difference). The moisture content of the as-received coal was 3.7%. Because this coal contains low levels of pyrite, the influence of native catalyst precursors is minimized.

Microautoclave liquefaction experiments were performed according to previously described procedures in 316-stainless-steel microautoclaves of approximately 46 cm³ internal volume (1). Separate microautoclaves were used for thermal and catalytic experiments to avoid residual catalytic effects. In the experiments reported here, 6.6 g of coal was used along with a hydrogen/3% hydrogen sulfide gas mixture at 7.2 MPa (1030 psig) cold pressure. In catalytic experiments, $\text{Mo}(\text{CO})_6$ was used as the catalyst precursor and was simply added to the microautoclave along with the coal at a level of 1000 ppm Mo based on daf coal. Slow heat-up to a reaction temperature of 375°C and a rapid cool-down were employed. The heat-up time was approximately 55 min. Residence times at temperature of 0, 30, and 60 min were used. All experiments were performed at least in duplicate and the respective products combined to prepare sufficient quantities for subsequent characterization. The products were recovered according to the referenced procedures (1).

Elemental analyses of the liquefaction products were performed at Huffman Laboratories in Golden, Colorado. Extensive characterization of the unreacted coal and the THF-insoluble liquefaction products was performed. This included solid-state ^{13}C NMR spectra, obtained at Western Research Institute in Laramie, Wyoming, following published procedures (2). Oxygen speciation analyses were also performed at PETC. The total hydroxyl contents of the coal and THF-insoluble products were determined by potentiometric titration following reaction with tetrabutylammonium hydroxide. Carboxylic acid contents were determined by exchange with barium ions under nitrogen and in a precisely calibrated buffer solution. The barium was then reacted with standard perchloric acid which was back-titrated to determine the extent of ion exchange. Petrographic analyses were also performed at PETC. The vitrinite reflectance measurements were performed on the vitrinite particles in the raw coal and 0-min residence time samples and on vitroplast (particles derived from heated vitrinite) in the 30-min and 60-min residence time samples according to ASTM procedure D 2798-91.

RESULTS AND DISCUSSION

In prior work with $\text{Mo}(\text{CO})_6$ and the DECS-17 coal, the onset of a catalytic effect on hydrogen uptake was detectable at 325°C. The rate of hydrogen uptake due to the catalyst became more pronounced near 370°C (1). In 1-h residence time experiments, the presence of the catalyst promoted conversion of the coal to THF- and cyclohexane-soluble products at temperatures above 325°C and 375°C, respectively. To further define the role of the catalyst, experiments have been conducted at 375°C at residence times of 0, 30, and 60 minutes. This temperature is slightly above that where the pronounced hydrogen uptake caused by the catalyst was observed. To prepare sufficient quantities of material for characterization, twice the usual amount of coal was used. The catalyst loading and initial hydrogen pressure remained the same.

Figure 1 contains the conversion results obtained for the recent experiments with 6.6 g of coal, as well as respective conversions from the previous 1-h experiments at 375°C in which 3.3 g of coal was used. Part A contains the thermal conversions, Part B the catalytic conversions, and Part C the data obtained after subtraction of the thermal conversions from the catalytic data at each residence time. All thermal and catalytic experiments were performed at least in duplicate. The bars on the data in parts A and B represent the range of values obtained and are shown if they are larger than the size of the symbol.

No improvements in the conversions attributable to the catalyst are observed in Figure 1 (part C) after the heat-up to reaction temperature (0 residence time). At the longer times, the catalyst is effective in promoting conversion to THF-soluble products; however, a definite catalytic effect is only observed at the longest reaction time with respect to cyclohexane conversion. With the smaller coal charge, no significant improvement in cyclohexane conversions was noted at 60 minutes. However, at a longer residence time of 8 h (not shown here), a catalytic effect was observed (1). A smaller but significantly lower catalyst-promoted THF conversion was also noted for the liquefaction of the smaller coal charge (part C of Figure 1). This latter observation appears to be due to the lower thermal conversion for the larger coal sample (part A of Figure 1), indicating that in the absence of catalyst, more retrogressive reactions occurred in the larger coal mass. However, with catalyst, the THF conversions were nearly the same for both coal amounts. This highlights the efficacy of the $\text{Mo}(\text{CO})_6$ precursor in forming a highly dispersed, active coal liquefaction catalyst.

A procedure has been developed that uses the pressure and temperature data recorded throughout the experiment to monitor the change in gas content of the reactor during solvent-free liquefaction experiments. A description of the procedure used to obtain this representation of the data has been published (1). Figure 2 contains these data for the current 1-h work and for the prior work with 3.3 g of coal. The prior work also showed that the catalyst had little effect on the gases liberated. Therefore, the thermal components, mainly liberation of CO , CO_2 , and hydrocarbon gases, have been subtracted from catalytic data to obtain the curves shown in Figure 2 which therefore primarily reflect the hydrogen uptake as a function of time and temperature. The only other major influence on the data in this figure that is unaccounted for is the liberation of water vapor from reactions associated with the catalyst.

Table 1 compares temperatures of the onset of gas uptake, both initial and rapid, and the initial rates of rapid gas uptake obtained from the data in Figure 1.

Table 1. Onset of catalytic activity and rates of gas uptake due to the catalyst for experiments at 375°C with various amounts of DECS-17 coal.

	Amount of Coal	
	3.3 g	6.6 g
Onset of Catalyst Activity, °C	345	335
Onset of Rapid Gas Uptake, °C	360	365
Initial Rate of Rapid Gas Uptake, $\text{mmol g}^{-1}(\text{daf coal}) \text{ min}^{-1}$	0.084	0.106

The conversion data and the data in Table 1 show that doubling the loading of the coal had little effect on reactivity. The total pressure in the microautoclave upon reaching reaction temperature with 6.6 g coal charged was about 11.9 MPa (1710 psig) and the total reduction in pressure after

1 h was 1.2 MPa (170 psi). Thus, a pseudo first-order condition with a nearly constant hydrogen partial pressure was maintained even in the case of greatest hydrogen demand.

The change in the slope of the curves shown in Figure 2 during the reaction at 375°C suggests that two major catalytic events are occurring during the course of the liquefaction reaction. This is most evident in the data for the reaction using 6.6 g of coal. Near the end of the heat-up period and for about 15 minutes into the reaction at 375°C, the rate of gas uptake is rapid. After this, the rate of gas uptake drops by about one-third to $0.31 \text{ mmol g}^{-1}(\text{daf coal}) \text{ min}^{-1}$. The change in the apparent rate of hydrogen consumption could be due to different time constants for the various reactions occurring in the liquefaction process. It was observed in thermal experiments that the generation of gas, primarily CO_2 at this temperature, was confined mainly to the early part of the reaction. The release of this gas has been associated with the onset of thermal reactions in the coal which can lead to a more refractory product in the absence of catalyst (3). The high hydrogen demand in the early part of the reaction may be due to the capping of the radicals generated by these thermal reactions. After this event, the lower hydrogen demand could be due to capping of radicals formed from the thermal reactions which occur in parallel with those responsible for the initial burst of activity. This hypothesis is in accord with the idea of an equilibrium between a radical pool and a reactive insoluble product recently used by Suzuki to model the liquefaction of a low-rank coal (4). The catalyst undoubtedly has other roles, especially in the later parts of the liquefaction process. These include heteroatom removal, hydrogenation of aromatic systems, and hydrocracking reactions; all of which would lead to the increase in the lighter, cyclohexane-soluble products observed after 60 minutes (part C of Figure 1).

To obtain additional information on the role of the catalyst, a detailed characterization of the THF-insoluble products from the reactions at 0, 30, and 60 min was performed. The following analytical techniques were used: organic petrography, ^{13}C solid-state NMR, an oxygen speciation technique developed at PETC, and elemental analysis.

Figure 3 shows the change in the H/C ratio and the vitrinite reflectance as a function of conversion of the coal to THF-soluble products. The THF conversion increased with residence time (see Figure 1); however, little change occurred after 30 min in the thermal experiments. The vitrinite reflectance values were determined as part of the petrographic examination of the vitrinite in the raw coal and the vitrinite or vitroplast in the THF-insoluble products. H/C data were also obtained for the same samples and for a sample of the raw coal that had been extracted with THF using the same procedure as for recovering the insoluble residue. The data show that hydrogen is added to the residue in the presence of the catalyst and that the H/C ratio is maintained at a level near that observed for the THF-extracted coal even up to a reaction time of 30 minutes (part A of Figure 3). Without catalyst, the H/C ratio drops even for the 0-residence time sample. The vitrinite reflectance measurements shown in part B of Figure 3 indicate that using catalyst results in a product that is less aromatic and therefore more reactive than in the thermal cases. Even for the 0-residence time sample, the presence of the catalyst resulted in a reflectance value at or even less than that of the starting coal. As with the H/C data, most of the changes in the thermal samples occur within the first 30 minutes at reaction temperature.

The THF-insoluble products obtained from the 0-min residence time experiments still consisted of identifiable macerals. The catalytic samples contained vitrinite particles that exhibited rounding of the edges which may indicate that the catalyst was promoting the initiation of coal softening. Catalytic hydrogenation has been observed to lower the initial softening temperature of coal and extend its plastic range (3). Vitrinite reflectance measurements were also recorded at the centers and edges of the vitrinite particles. In the thermal samples, the reflectance measurements were nearly constant across the particles (0.70% center, 0.69% edge). The values for the catalytic samples were substantially lower and there was a slight increase in vitrinite reflectance from the edge areas (0.58%) to the center (0.61%). Similar observations have been reported in the literature for coal liquefied using naphthalene as a solvent (5). The petrographic and elemental analyses show that, even though the catalyst had not affected the yields of THF-soluble products at 0-min residence time, significant changes had already been induced in the coal by its presence.

The inferences drawn from petrographic and elemental analyses were strengthened by additional information provided by solid-state ^{13}C NMR, summarized in Figure 4. At the onset of liquefaction, the presence of the catalyst limited the increase in the fraction of aromatic carbons in the THF-insoluble product (part A of Figure 4) as compared to the thermal product. This

corroborates the vitrinite reflectance measurements shown in part B of Figure 3. With time, this effect became more pronounced. At the longer reaction times, the catalyst exerted a definite effect on limiting the growth of aromatic clusters in the insoluble product (part B of Figure 4). The presence of the catalyst also resulted in lower attachments per average cluster (part C of Figure 4) and lower molecular weights of the clusters with respect to the amount of conversion that occurred. Liquefaction creates a hydrogen demand that is partially satisfied in the thermal case by condensation and aromatization reactions in the residue. The catalyst provides an alternate source of hydrogen from the gas phase, thus resulting in less condensation and aromatization in the residue.

The effect of catalyst on the oxygen-containing species present in the THF-insoluble products is made evident by the data assembled in Figure 5 from elemental, NMR, and oxygen speciation analyses. Part A contains the atomic O/C ratios as a function of conversion. Only small overall changes are noted and no overall concentration of oxygen-containing species was apparent as more of the coal liquefied. The NMR data in part B and the results of oxygen speciation analyses in part C show that initially the amounts of hydroxyl or phenolic substituted carbon in the THF-insoluble products were similar to that in the starting material. Also, based on data from the potentiometric titrations (not shown), the relative proportion of strong acids in the THF-insoluble products from reactions with catalyst increased. Without catalyst little change was noted.

After 30-min reaction time in the absence of catalyst, the unconverted material does not change in regard to oxygen content or speciation. This is in marked contrast to the extensive increase in aromaticity seen in Figure 4. Catalyst does not seem to have a profound effect on oxygen distribution with the exception that the number of hydroxyl and phenolic substituted carbons becomes somewhat more concentrated in the small fraction of coal left unconverted.

Part D of Figure 5 contains additional information derived from the oxygen speciation analysis and shows that the presence of the catalyst resulted in a small but definite increase in the amount of carboxyl groups in the THF-insoluble products. Virtually no change was observed in the products from the thermal experiments. The carboxyl groups are not formed during the liquefaction reaction but rather through aerial oxidation of the residues during the workup procedure. Catalytic liquefaction apparently renders the remaining residues more susceptible to such oxidation.

CONCLUSIONS

Solvent-free liquefaction with a well-dispersed catalyst provides an excellent opportunity to study its effects on coal without the complications generated by excess extraneous material. The results presented here show that a low level of catalyst addition significantly promotes conversion and the uptake of hydrogen from the gas phase even in the early stages of the liquefaction process. Even before the yields of THF-soluble products are affected, the catalyst causes significant changes in the coal. Petrographic analysis of the liquefaction residues indicates the catalyst promotes hydrogenation and softening. Solid-state ^{13}C NMR analysis reveals pronounced differences between thermal and catalytic residues. The former are more aromatic, contain more aromatic carbons per cluster, and more attachments per cluster. A net effect of catalyst is to protect the unconverted material from thermal reactions leading to the formation of a highly aromatic char. At the conditions of these experiments, reactions involving oxygen functionalities did not seem to be greatly affected by the presence of the catalyst.

ACKNOWLEDGMENTS AND DISCLAIMER

The authors would like to thank Richard Hlasnik and Jerry Foster for performing the microautoclave work. The NMR analyses were performed by Dr. Francis Miknis and Dr. Daniel Netzel of the Western Research Institute in Laramie, Wyoming. Reference in this report to any specific product, process, or service is to facilitate understanding and does not imply its endorsement or favoring by the United States Department of Energy.

REFERENCES

1. R.P. Warzinski; B.C. Bockrath *Energy & Fuels* 1996, 10, 612-622.
2. M.S. Solum; R.J. Pugmire; D.M. Grant *Energy & Fuels* 1989, 3, 187-193.
3. F.J. Derbyshire; A. Davis; R. Lin *Energy & Fuels* 1989, 3, 431-437.
4. T. Suzuki *Energy & Fuels* 1994, 8, 341-347.
5. F.J. Derbyshire; A. Davis; M. Epstein; P. Stansberry *Fuel* 1986, 65, 1233-1239.

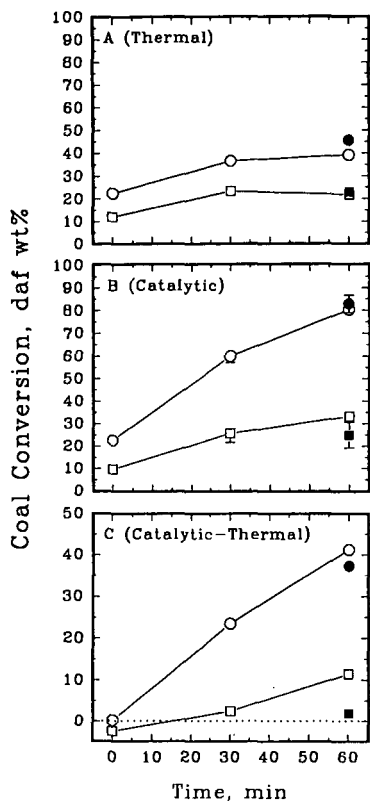


Figure 1. Conversion results for 375°C experiments with DECS-17 coal. (○, ●) THF conversion; (□, ■) cyclohexane conversion. Open symbols - 6.6 g coal; closed symbols - 3.3 g coal.

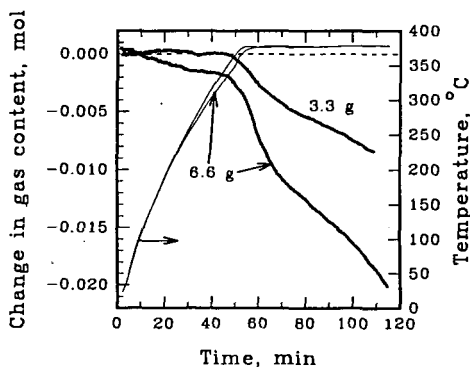


Figure 2. Effect of coal loading on changes in gas content in the microautoclave due to the catalysts for 1-h experiments with DECS-17 coal.

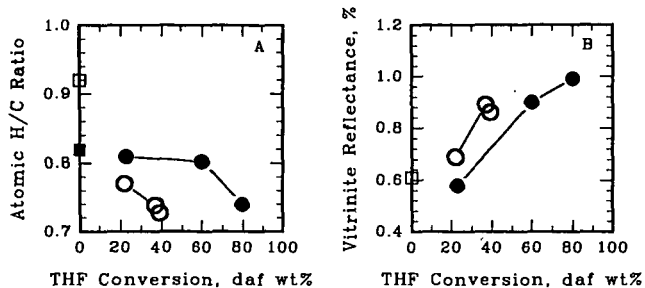


Figure 3. Vitrinite reflectance data and atomic H/C ratios for THF insols from experiments at 375°C with DECS-17 coal. (○ thermal; ● catalytic; □ untreated coal; ■ untreated, THF-extracted coal.)

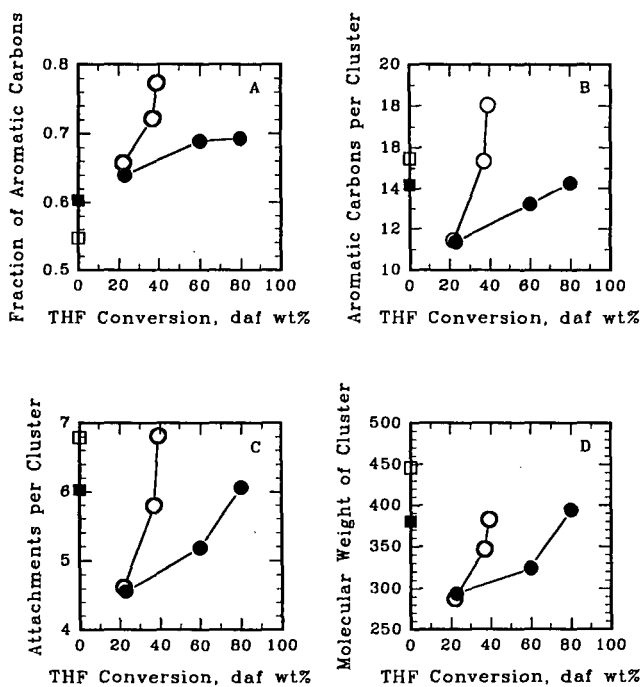


Figure 4. Solid-state ^{13}C NMR data for THF insols from experiments at 375°C with DECS-17 coal. (Symbol definitions are the same as in Figure 3.)

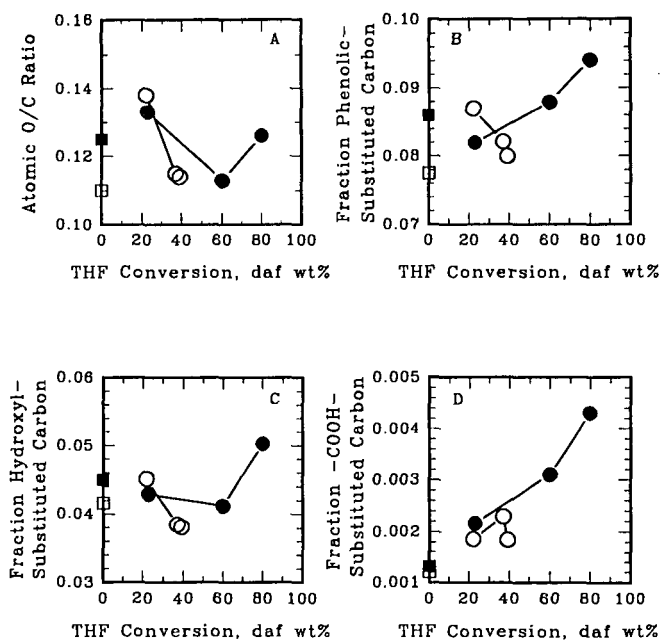


Figure 5. Oxygen species data for THF insols from experiments at 375 °C with DECS-17 coal. (Symbol definitions are the same as in Figure 3.)